

Carrier Density Dependence of the Magnetic Properties in Iron-doped Bi_2Se_3 Topological Insulator

H. Li,¹ Y. R. Song,¹ Meng-Yu Yao,¹ Fengfeng Zhu,¹ Canhua Liu,¹ C. L. Gao,¹ Jin-Feng Jia,¹ Dong Qian,^{1, a)} X. Yao,¹ Y. J. Shi,² and D.Wu²

¹⁾*Key Laboratory of Artificial Structures and Quantum Control (Ministry of Education), Department of Physics, Shanghai Jiao Tong University, Shanghai 200240, China*

²⁾*The National Laboratory of Solid State Microstructures (NLSSM), Nanjing University, Nanjing, 210093, China*

The electronic and magnetic properties of iron-doped topological insulator $\text{Bi}_{1.84-x}\text{Fe}_{0.16}\text{Ca}_x\text{Se}_3$ single crystals were studied. By co-doping Fe and Ca atoms, ferromagnetic bulk states with different carrier density (from n-type to p-type) were obtained. Effective magnetic moments for each Fe atom was estimated as small as about $0.07\mu_B$. Magnetic and non-magnetic phase separation was observed in all samples. Our results suggest that the bulk ferromagnetism in Fe-doped Bi_2Se_3 is not intrinsic and regardless of carrier density.

^{a)}Electronic mail: dqian@sjtu.edu.cn

I. INTRODUCTION

Distinguished from trivial insulators, topological insulators (TIs) - a new state of quantum matter - possessing gapless topological edge states protected by time reversal symmetry (TRS) have been attracting extensive studies recently¹⁻¹⁴. A number of materials have been proved or proposed to be TIs including Hg(Cd)Te quantum well⁴, $\text{Bi}_{1-x}\text{Sb}_x$ alloys⁷, binary compounds (Bi_2Se_3 , Bi_2Te_3 , Sb_2Te_3)^{8-10,12}, Half-Heusler compounds^{15,16}, ultra-thin Bi(111) bilayers^{14,17} and so on. Among these materials, Bi_2Se_3 is thought to be the most promising three dimensional TI for potential applications because of its simplest single helical Dirac cone surface states and the largest bulk gap (300meV)^{7,8}. An energy gap can be opened at Dirac point to form massive Dirac Fermion by introducing TRS breaking field, such as magnetic field. Similar to graphene, opening an energy gap in the Dirac cone is very important for potential applications. In addition, the interplay between ferromagnetic states and topological states can cause many exotic phenomenon such as magnetic monopole, anomalous quantum Hall effect and the topological properties related Faraday and Kerr magneto-optical effects¹⁸⁻²⁰. Ferromagnetic states have been observed in 3d transitional magnetic elements (V, Cr, Mn, Fe) doped Bi_2Te_3 , Bi_2Se_3 , Sb_2Te_3 single crystals or films²¹⁻²⁹. Massive Dirac Fermion will form when the magnetic moments have component perpendicular to the surface. In those magnetic TIs, the expected massive Dirac Fermion was only observed in Fe-doped and Mn-doped Bi_2Se_3 using angle-resolved photoemission spectroscopy (ARPES)^{30,31}. Though, the observed energy gap at Dirac point is very large ($\sim 60\text{meV}$), the bulk magnetic properties of $\text{Fe}_x\text{Bi}_{2-x}\text{Se}_3$ are still controversial^{30,32,33}. At the same time, the Fermi level is not within the gap³⁰ either. In the first report which claimed the observation of the massive Dirac Fermion³⁰, high Curie temperature (T_c) and small total magnetic moments were observed. Assuming doped Fe atoms have a valence of +3, only few Fe ($x=0.002 - 0.005$) atoms are estimated to enter the material matrix with a nominal concentration of $x=0.1$ to $x=0.3$. Intergrowth of Bi_2Se_3 and magnetic Fe_xSe_y phase was also observed in some samples³³. In another experiment³², Fe atoms were thought to completely enter the material matrix and make Fe-doped Bi_2Se_3 be intrinsic ferromagnetic semiconductor. Since Bi_2Se_3 is a semiconductor, in principle, intrinsic ferromagnetic TI would have similar magnetic behavior as the well-defined diluted magnetic semiconductor such as $(\text{Mn,Ga})\text{As}$ ^{34,35}. If the ferromagnetic states in Fe-doped Bi_2Se_3 is intrinsic, the over-

all magnetic properties should strongly depend on the carrier density. On the other hand, in some systems, dopants with different valance can destroy the formation of ferromagnetic clusters³⁶. It is very important to carry out the carrier dependent experiments on Fe-doped Bi_2Se_3 systems for several reasons: i)To understand the origin of the bulk ferromagnetic states. ii)To control its magnetic properties. iii)To move the Fermi level into the gap near the Dirac point.

In this work, we carefully studied the magnetic properties of Fe-doped Bi_2Se_3 with Fe concentration of $x=0.16$ where the energy gap at Dirac point was nearly saturated³⁰ as a function of carrier density. We succeeded in tuning the Fermi level to Dirac point with proper mount of Ca doping. For all Ca doped samples, ferromagnetic states were obtained. However, magnetic and non-magnetic phases separation existed in all samples. The magnetic properties could not be tuned systematically by carrier density. Regardless the carrier density, bulk ferromagnetism mainly came from extrinsic magnetic clusters.

II. EXPERIMENT

High quality single crystals of $\text{Bi}_{1.84-x}\text{Fe}_{0.16}\text{Ca}_x\text{Se}_3$ ($x=0, 0.02, 0.04, 0.06$) were grown by modified Bridgman method³⁰. High purity of Bi (99.999%), Fe (99.999%), Ca (99.5%) and Se (99.999%) powders were carefully mixed and sealed in evacuated quartz tubes. Excess amount of selenium was used to reduce the selenium vacancy. The tubes were firstly heated to 850°C and kept for 24 hours, then slowly cooled to 550 °C within 2 days, followed by 3 days annealing. The obtained crystals were well crystallized and could be easily cleaved perpendicular to the c-axis. The concentration of Fe and Ca dopants in the crystals were carefully determined by inductively coupled plasma (ICP) (iCAP THERMO 6000 Radial). The band structures were measured by ARPES with 10 eV photons at 77K in National Synchrotron Radiation Laboratory (NSRL, Hefei) using Scienta R4000 analyzer with base pressures better than 5×10^{-11} Torr. Hall measurements were carried out in the Magnetocryostat (Oxford). Magnetic measurements were performed by Physical Property Measurement System (PPMS) (Quantum Design) with magnetic field paralleled or perpendicular to the c-axis of the samples. ICP analysis shows that almost all of the nominal Fe atoms incorporated into the crystals. Though not all the Ca can enter the crystals, Ca concentration increases with x , approximately (Table-1). The maximum Ca entered into the

crystals we obtained is about $x_{eff}=0.018$.

III. RESULTS AND DISCUSSION

As-grown Bi_2Se_3 crystals show electron doping (n-type) due to the intrinsic Se vacancies^{9,37}. Altering the Bi:Se ratio in the nominal composition can reduce the defects to a certain extent, however, can not change the carrier type. If Fe atoms enter the Bi-Se matrix, they can occupy two possible positions in the crystal. The first possibility is that Fe atoms substitute Bi atoms with the same valence of +3, thus it will hardly change the carrier density^{19,30,38}. This kind of substitution happens in other doped topological insulators^{26,29,39}. Another possibility is Fe intercalation in the Van der Waals space between two quintuple layers. In this case, Fe atoms will supply additional electrons into Fermi sea^{40,41}. Figure 1 (a)-(d) present the low energy electronic structures of $\text{Bi}_{1.84-x}\text{Fe}_{0.16}\text{Ca}_x\text{Se}_3$ measured by ARPES at 77K. Linearly dispersive surface states are clearly observed in all samples. Similar to the reported Fe-doped samples³⁰, the Dirac point of surface states locates at ~ 200 meV below the Fermi level without Ca doping. Fermi level touches the bottom of conduction bands. In Bi_2Se_3 single crystals, the Dirac point locates at about 200-350 meV below the Fermi level depending on the initial ratio of Bi and Se. Known from the ARPES results, Fe does not act as an electron donor in our samples, which indicates that there is very little Fe intercalation. Each Ca atom can substitute Bi atom in the form of Ca^{2+} and supplies a hole into the Fermi sea¹⁰, so with the increase of Ca doping levels the Fermi level moves downward. Fermi level is tuned to the position that is very close the Dirac point(Fig. 1(d)) when the Ca nominal doping is $x=0.06$. Figure 1 (e) and (f) show the energy distribution curves (EDCs) near the Dirac points for $x=0$ and $x=0.02$, respectively. Blue curves are the EDCs at $k=0$. Spectral weight suppression ("gap"-like) at Dirac point were clearly observed on $x=0$ and $x=0.02$ samples. Seen from Fig. 1(e) and (f), though the energy resolution is not as good as the reference [30], two peaks in EDC (blue curve) were observed which is very similar to the previous report³⁰. For $x=0.04$ and 0.06 samples, because of the doping induced disorder, the spectra is not sharp enough to observe spectral weight suppression. The gap we observed in $x=0$ and $x=0.02$ samples is about 50 to 90 meV depending on samples that is close to the gap value in reference [30]. However the "gap"-like feature is not the sole evidence of the formation of long-range intrinsic ferromagnetism. In fact, "gap"-like feature was observed

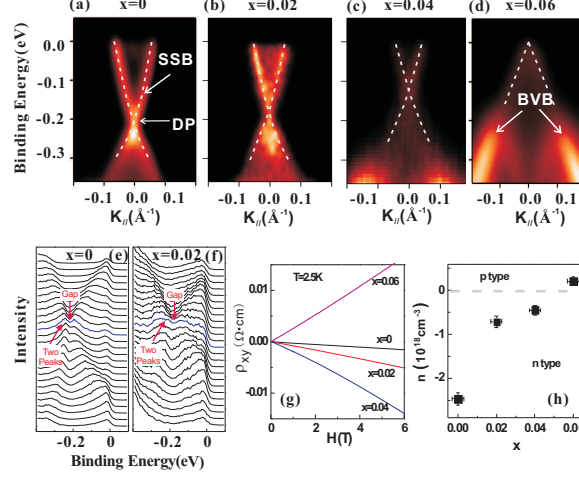


FIG. 1. Low energy ARPES spectra of $\text{Bi}_{1.84-x}\text{Fe}_{0.16}\text{Ca}_x\text{Se}_3$ with (a) $x=0$, (b) $x=0.02$, (c) $x=0.04$, (d) $x=0.06$. Fermi level moves downwards to the Dirac point with the increase of Ca dopants. (e)EDCs near the Dirac point for $x=0$ and (f) $x=0.02$. Blue curves are EDCs at $k=0$. (g) Hall resistivity as a function of applied magnetic filed. (h) Carrier density as a function of Ca concentration.

in many topological insulators with magnetic or non-magnetic doping recently⁴². We can not make conclusion on the magnetic states based on the ARPES results. ARPES measurement is surface sensitive, which can give the information of the carrier density near the surface region. The bulk carrier density as a function of Ca doping was further measured by Hall effects. Figure 1(g) presents the Hall resistivity as a function of applied magnetic field. Figure 1(h) shows the carrier density extracted from Fig. 1(g) as a function of Ca concentration. The reported carrier density of Bi_2Se_3 varies from $\sim 10^{19} \text{ cm}^{-3}$ to $\sim 10^{17} \text{ cm}^{-3}$ obtained by different groups^{43–45} depending on the initial stoichiometry of Bi and Se and the preparing methods. In our parent compound $\text{Bi}_{1.84}\text{Fe}_{0.16}\text{Se}_3$, the measured carrier density is about $2.5 \times 10^{18} \text{ cm}^{-3}$ which is consistent with previous reports. Consistent with ARPES measurements, the incorporation of Ca into the crystals reduces the electron density and drives the carrier change from n-type to p-type. By co-doping Fe and Ca, we successfully tuned the Fermi level to the Dirac point. The successful tuning of the carrier concentration also allows us to explore the relation between magnetic properties and carrier density.

For all the samples, bulk ferromagnetism is observed at 2.1K. Figure 2 (a) and (b) show the magnetic moments (M) as a function of temperature (T) for different Ca concentrations with magnetic field perpendicular or parallel to the c-axis, respectively. Under the applied

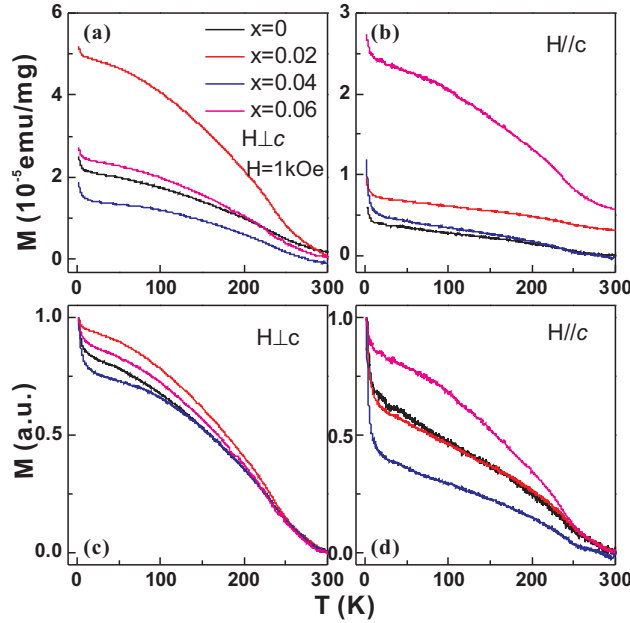


FIG. 2. Field cooled temperature dependent dc magnetism with an applied field of 1kOe for the $\text{Bi}_{1.84-x}\text{Fe}_{0.16}\text{Ca}_x\text{Se}_3$ crystals along (a) in-plane, (b) out-of-plane, (c) in-plane after normalization, (d) out-of-plane after normalization.

magnetic field (1kOe), the amplitude of the magnetic signal varies for different Ca concentration, however, they show similar T-dependent behavior. Figure 2 (c) and (d) present the M-T curves after being normalized by the signals at the lowest temperature (2.1 K). In other magnetic topological insulators, like Cr-doped Sb_2Te_3 ^{26,29} and Mn-doped Bi_2Te_3 ²², only single magnetic transition point was observed. However, in Fe-doped Bi_2Se_3 , there are three possible turn points in the M-T curves – at about 10K, 100K to 200K and 250K to 300K, similar to previous results^{30,32}. This implies the magnetic properties in this system are much more complicated.

In order to find the origin of the magnetic signals in Fe-doped Bi_2Se_3 , we further systematically studied the magnetic hysteresis loops (M-H curves) along the in-plane direction as a function of carrier density. Figure 3 present M-H curves of samples with different Ca concentrations. The M-H curve of Bi_2Se_3 sample shows pure diamagnetic behavior, which does not show any noticeable change by small amount of Ca-doping. The blue curves present diamagnetic signals from the parent compounds without Fe. With Fe doping, there are clear hysteresis loops at 2.1K which indicates the existence of ferromagnetic state. Seen from Fig.

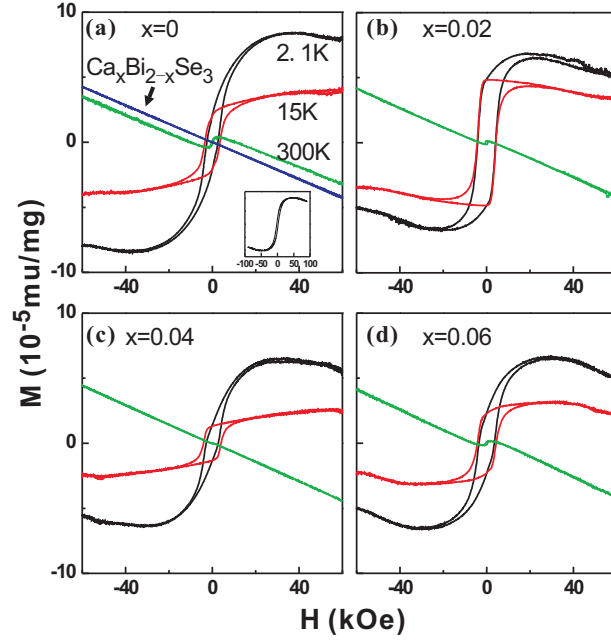


FIG. 3. The Magnetic hysteresis loops along the in-plane direction at different temperature for (a) $x=0$, (b) $x=0.02$ (c) $x=0.04$, (d) $x=0.06$

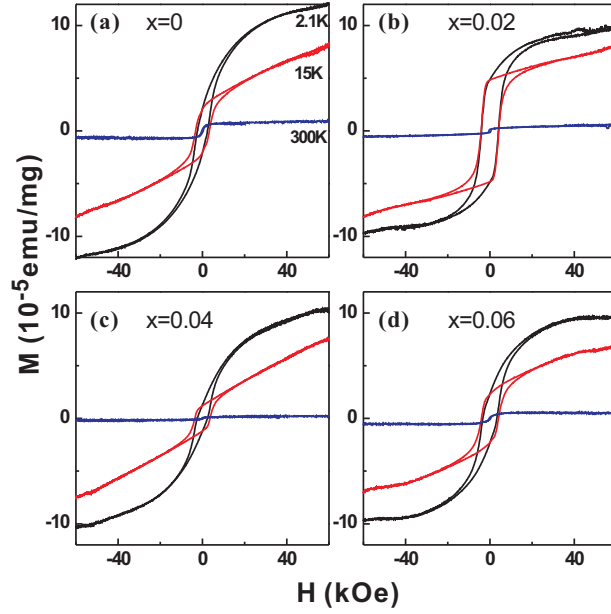


FIG. 4. The Magnetic hysteresis loops along the in-plane direction at different temperatures after subtracting the diamagnetic signals for (a) $x=0$, (b) $x=0.02$ (c) $x=0.04$, (d) $x=0.06$

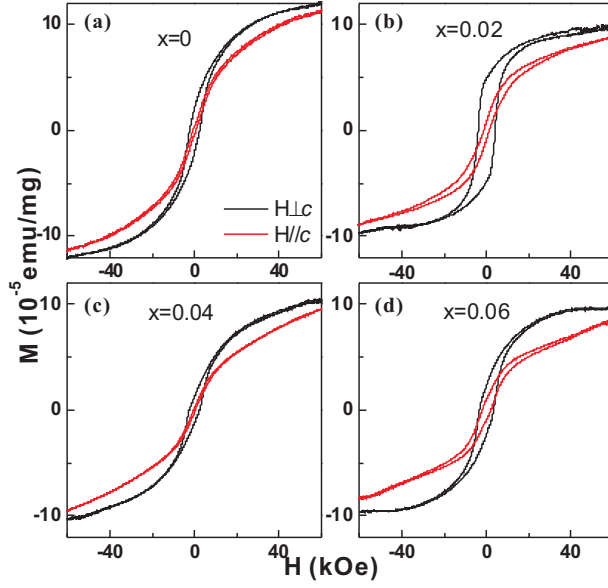


FIG. 5. Comparison of the magnetic hysteresis loops along the out-of-plane and in-plane directions after subtracting the diamagnetic signals for (a) $x=0$, (b) $x=0.02$ (c) $x=0.04$, (d) $x=0.06$

3(a), the magnetic signal is nearly saturated at about 40 KOe and a diamagnetic signal appears again at high magnetic field. Insert in Fig. 3(a) presents the magnetic signal up to 90 KOe. Diamagnetic signals are much clearer at high field. The estimated diamagnetic susceptibility is about $7.1 \times 10^{-6} \text{ emu}/(\text{g} \cdot \text{T})$ which is close to that of pure Bi_2Se_3 . Similar diamagnetic signals are also obvious in Ca-doped samples (Fig. 3(b)-(d)). The existence of the diamagnetic signal implies that there is phase separation of non-magnetic Bi_2Se_3 or Ca-doped Bi_2Se_3 phase and magnetic phase. In Figure 4, We subtract the diamagnetic signals from the total signals to get the pure magnetic signals that related to the magnetic phase with Fe dopants. The overall M-H curves become simple. See from Fig. 5, at 2.1K, at zero field, the remanent magnetization is larger along the in-plane direction, which means the magnetic moments intend to stay in plane.

For all the samples, the pure magnetic signals are nearly saturated at 60 KOe. Using the signal measured at 60 KOe and ICP results, we calculated the average magnetic moments of per Fe atom as shown in Table 1. For all samples, the calculated magnetic moments per Fe atom are very close. It is about $0.07 \pm 0.02 \mu_B$ which is much smaller than possible magnetic moments of Fe^{3+} ion. Such small magnetic moment can not be explained by the scenario of Fe substitution of Bi. Actually, first principle calculation¹⁹ assuming Fe substitution of

TABLE I. Concentrations of doped Ca and Fe and the magnetic moments for different magnetic dopants

x	Fe	Ca	$n(\text{cm}^{-3})$	$M_{6T}(\mu_B/F e_{atom})$
0	0.16 ± 0.02	0	-2.47×10^{18}	0.08 ± 0.01
0.02	0.19 ± 0.02	0.009 ± 0.005	-7.04×10^{17}	0.07 ± 0.01
0.04	0.16 ± 0.02	0.012 ± 0.005	-4.46×10^{17}	0.06 ± 0.01
0.06	0.14 ± 0.02	0.018 ± 0.005	2.14×10^{17}	0.06 ± 0.01

Bi gave high spin states of Fe atoms. Since the magnetic properties of Fe-doped Bi_2Se_3 do not obviously depend on the carrier density, we conclude that the most part of the magnetic signals is extrinsic. They are not diluted ferromagnetic semiconductors. We can exclude the formation of Fe inclusions. If the ferromagnetism comes from Fe inclusions, we should get large average magnetic moments per Fe atoms ($2.2\mu_B/\text{atom}$ for bulk Fe). On the other hand, Fe and Se can form complicated compounds Fe_xSe_y ^{46,47} which present ferrimagnetic and/or antiferromagnetic behaviors. According to previous report on bulk Fe_xSe_y compounds⁴⁷, the value of magnetic moment of Fe atom in Fe_xSe_y varies depending on the exactly ration of Fe and Se. The reported minimum value is from 0.2 to $0.4 \mu_B$ and has the same order of magnitude as our results. So we think that the magnetic phase in our Fe-doped Bi_2Se_3 samples could be some forms of Fe_xSe_y nanocrystals. Two possible explanation on the very small magnetic momentum. First, those nanocrystals are ferrimagnetic with low spin states. Second, they can be in antiferromagnetic states with uncompensated surface spins that gives the small ferromagnetic signals. Since our finding is based on bulk measurement, we can not exclude some intrinsic ferromagnetism on the surface which may open a real gap in ARPES spectra.

IV. CONCLUSIONS

By co-doping Ca and Fe, we succeeded in tuning the carrier density from n-type to p-type in ferromagnetic $\text{Bi}_{1.84-x}\text{Fe}_{0.16}\text{Ca}_x\text{Se}_3$ samples. We studied the evolution of the magnetic properties as a function of carrier density. Contrast to well-defined ferromagnetic semiconductor, the magnetic properties in Fe-doped Bi_2Se_3 do not have obvious dependence on the

carrier density. Our results suggest that the bulk ferromagnetic behaviors of Fe-doped Bi_2Se_3 are due to Fe_xSe_y nanoclusters in the crystals. In principle, the nature of the gap observed near Dirac point could be solved by determining the spin polarization using spin-resolved ARPES or spin-polarized scanning tunnelling spectroscopy in the future.

V. ACKNOWLEDGMENTS

We thank Z. Sun and G. B. Zhang from National Synchrotron Radiation Laboratory of China for help on ARPES measurement. This work is supported by National Basic Research Programm of China (Grant No. 2012CB927401, 2011CB921902, 2013CB921902, 2011CB922200), NSFC (Grant No. 91021002, 11174199, 11134008, 11274228), Shanghai Committee of Science and Technology, China (No. 11JC1405000, 11PJ1405200, 12JC1405300), Shanghai Municipal Education Commission (11ZZ17) and SRF for ROCS, SEM. D.Q. acknowledges additional support from Programm for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning.

REFERENCES

- ¹M. Z. Hasan, C. L. Kane, Rev. Mod. Phys. **82**, 3045 (2010).
- ²Xiao-Liang Qi and Shou-Cheng Zhang, Rev. Mod. Phys. **83**, 1057 (2011).
- ³B. A. Bernevig, T. L. Hughes, and S.C. Zhang, Science, **314**, 1757 (2006).
- ⁴M. König, S. Wiedmann, C. Brüne, A. Roth, H. Buhmann, L.W. Molenkamp, X.L. Qi, and S.C. Zhang, Science **318**, 766 (2007).
- ⁵L. Fu, C. L. Kane, Phys. Rev. B **76**, 045302 (2007).
- ⁶J. E. Moore, and L. Balents, Phys. Rev. B **75**, 121306(R) (2007).
- ⁷D. Hsieh, D. Qian, L. Wray, Y. Xia, Y. S. Hor, R. J. Cava and M. Z. Hasan, Nature **452**, 970 (2008).
- ⁸H. J. Zhang, C.X. Liu, X.L. Qi, X. Dai, Z. Fang, and S.C. Zhang, Nature Phys. **5**, 438 (2009).
- ⁹Y. Xia, D. Qian, D. Hsieh, L. Wray, A. Pal, H. Lin, A. Bansil, D. Grauer, Y. S. Hor, R. J. Cava, and M. Z. Hasan, Nature Phys. **5**, 398 (2009).

- ¹⁰Y. L. Chen, J. G. Analytis, J.H. Chu, Z. K. Liu, S.K. Mo, X. L. Qi, H. J. Zhang, D. H. Lu, X. Dai, and Z. Fang, *Science* **325**, 178 (2009).
- ¹¹D. Hsieh, Y. Xia, D. Qian, L. Wray, J. H. Dil, F. Meier, J. Osterwalder, L. Patthey, J. G. Checkelsky, N. P. Ong, A. V. Fedorov, H. Lin, A. Bansil, D. Grauer, Y. S. Hor, R. J. Cava, and M. Z. Hasan, *Nature* **460**, 1101 (2009).
- ¹²D. Hsieh, Y. Xia, D. Qian, L. Wray, F. Meier, J. H. Dil, J. Osterwalder, L. Patthey, A.V. Fedorov, H. Lin, A. Bansil, D. Grauer, Y. S. Hor, R. J. Cava, and M. Z. Hasan, *Phys. Rev. Lett.* **103**, 146401 (2009).
- ¹³Mei-Xiao Wang, Canhua Liu, Jin-Peng Xu, Fang Yang,¹ Lin Miao, Meng-Yu Yao, C. L. Gao, Chenyi Shen, Xucun Ma, X. Chen, Zhu-An Xu, Ying Liu, Shou-Cheng Zhang, Dong Qian, Jin-Feng Jia, Qi-Kun Xue, *Science* **336**, 52 (2012).
- ¹⁴Fang Yang, Lin Miao, Z. F. Wang, Meng-Yu Yao, Fengfeng Zhu, Y. R. Song, Mei-Xiao Wang, Jin-Peng Xu, Alexei V. Fedorov, Z. Sun, G. B. Zhang, Canhua Liu, Feng Liu, Dong Qian, C. L. Gao, and Jin-Feng Jia, *Phys. Rev. Lett.* **109**, 016801 (2012).
- ¹⁵Hsin Lin, L. Andrew Wray, Yuqi Xia, Suyang Xu, Shuang Jia, Robert J. Cava, Arun Bansil and M. Zahid Hasan, *Nat. Mater.* **9**, 546, (2010).
- ¹⁶Di Xiao, Yugui Yao, Wanxiang Feng, Jun Wen, Wenguang Zhu, Xing-Qiu Chen, G. Malcolm Stocks, and Zhenyu Zhang, *Phys. Rev. Lett.* **105**, 096404 (2010).
- ¹⁷Yoshinori Okada, Chetan Dhital, Wenwen Zhou, Erik D. Huemiller, Hsin Lin, S. Basak, A. Bansil, Y.-B. Huang, H. Ding, Z. Wang, Stephen D. Wilson, and V. Madhavan, *Phys. Rev. Lett.* **106**, 206805 (2011).
- ¹⁸Xiao-Liang Qi, Rundong Li, Jiadong Zang, Shou-Cheng Zhang, *Science* **323**, 1184 (2009).
- ¹⁹R. Yu, W. Zhang, H.-J. Zhang, S.-C. Zhang, X. Dai, and Z. Fang, *Science*, **329**, 61 (2010).
- ²⁰Wang-Kong Tse and A.H. MacDonald, *Phys. Rev. Lett.* **105**, 057401 (2010).
- ²¹J. Choi, S. Choi, J. Choi, Y. Park, H. Park, H. Lee, B. Woo, and S. Cho, *Phys. Status Solidi B* **241**, 1541 (2004).
- ²²Y. S. Hor, P. Roushan, H. Beidenkopf, J. Seo, D. Qu, J. G. Checkelsky, L. A. Wray, D. Hsieh, Y. Xia, S.-Y. Xu, D. Qian, M. Z. Hasan, N. P. Ong, A. Yazdani, and R. J. Cava, *Phys. Rev. B* **81**, 195203 (2010).
- ²³V. A. Kulbachinskii, A. Y. Kaminskii, K. Kindo, Y. Narumi, K. Suga, P. Lostak, and P. Svanda, *Physica B: Condens. Matter.* **311**, 292 (2002).
- ²⁴J. S. Dyck, P. Hájek, P.Lošt'ák and C. Uher, *Phys. Rev. B* **65**, 115212 (2002).

- ²⁵J. S. Dyck, P. Svanda, P. Hájek, J. Horak, W. Chen, and C. Uher, J. Appl. Phys. **94**, 7631 (2003).
- ²⁶J. S. Dyck, C. Drasar, P. Hájek and C. Uher, Phys. Rev. B **71**, 115214 (2005).
- ²⁷Z. Zhou, Y.-J. Chien, and C. Uher, Phys. Rev. B **74**, 224418 (2006).
- ²⁸P. P. J. Haazen, J.-B. Laloë T. J. Nummy, H. J. M. Swagten, P. Jarillo-Herrero, D. Heiman and J. S. Moodera, Appl. Phys. Lett. **100**, 082404 (2012)
- ²⁹H. Li, Y. R. Song, Meng-Yu Yao, Fang Yang, Lin Miao, Fengfeng Zhu, Canhua Liu, C. L. Gao, Dong Qian, X. Yao, Jin-Feng Jia, Y. J. Shi, and D. Wu, Appl. Phys. Lett. **101**, 072406 (2012).
- ³⁰Y. L. Chen, J.-H. Chu, J. G. Analytis, Z. K. Liu, K. Igarashi, H.-H. Kuo, X. L. Qi, S. K. Mo, R. G. Moore, D. H. Lu, M. Hashimoto, T. Sasagawa, S. C. Zhang, I. R. Fisher, Z. Hussain, Z. X. Shen, Science **329**, 659 (2010).
- ³¹Su-Yang Xu, Madhab Neupane, Chang Liu, Duming Zhang, Anthony Richardella, L. Andrew Wray, Nasser Alidoust, Mats Leandersson, Thiagarajan Balasubramanian, Jaime Sánchez-Barriga, Oliver Rader, Gabriel Landolt, Bartosz Slomski, Jan Hugo Dil, Jürg Osterwalder, Tay-Rong Chang, Horng-Tay Jeng, Hsin Lin, Arun Bansil, Nitin Samarth, and M. Zahid Hasan, Nature Physics **8**, 616 (2012).
- ³²Z. Salman E. Pomjakushina, V. Pomjakushin, A. Kanigel, K. Chashka, K. Conder, E. Morenzoni, T. Prokscha, K. Sedlak, and A. Suter. arXiv:1203.4850v1
- ³³Huiwen Ji, J. M. Allred, Ni Ni, Jing Tao, M. Neupane, A. Wray, S. Xu, M. Z. Hasan, and R. J. Cava, Phys. Rev. B **85**, 165313 (2012).
- ³⁴T. Jungwirth, J. Sinova, J. Masek, J. Kucera, and A. H. MacDonald, Rev. Mod. Phys. **78**, 809 (2006).
- ³⁵M. Sawicki, D. Chiba, A. Korbecka, Y. Nishitani, J. A. Majewski, F. Matsukura, T. Dietl, and H. Ohno, Nat. Phys. **6**, 22 (2010).
- ³⁶T. Dietl, J. Phys.: Condens. Matter **19**, 165204 (2007).
- ³⁷J. Navrátil, J. Horák, T. Plechacek, S. Kamba, P. Lošťák, J. S. Dyck, W. Chen, and C. Uher, J. Solid State Chem. **177**, 1704 (2004).
- ³⁸Y. Sugama, T. Hayashi, H. Nakagawa, N. Miura, and V. A. Kulbachniskii, Physica B **298**, 531 (2001).
- ³⁹Y. R. Song, Fang Yang, Meng-Yu Yao, Fengfeng Zhu, Lin Miao, Jin-Peng Xu, Mei-Xiao Wang, H. Li, X. Yao, Fuhao Ji, S. Qiao, Z. Sun, G. B. Zhang, B. Gao, Canhua Liu, Dong

- Qian, C. L. Gao, and Jin-Feng Jia, Appl. Phys. Lett. **100**, 242403 (2012).
- ⁴⁰L. Andrew Wray, Su-Yang Xu, Yuqi Xia, David Hsieh, Alexei V. Fedorov, Yew San Hor, Robert J. Cava, Arun Bansil, Hsin Lin, M. Zahid Hasan, Nature Physics **7**, 32 (2011).
- ⁴¹T. Valla, Z.-H. Pan, D. Gardner, Y. S. Lee, and S. Chu, Phys. Rev. Lett. **108**, 117601 (2012).
- ⁴²S.Y. Yu, L.A. Wray, N. Alidoust, Y. Xia, M. Neupane, C. Liu, H.-W. Ji, S. Jia, R.J. Cava, M.Z. Hasan, <http://arxiv.org/abs/1206.0278v3>.
- ⁴³Y.S. Hor, A. Richardella, P. Roushan, Y. Xia, J. Checkelsky, A. Yazdani, M. Hasan, N. Ong, and R. Cava, Phys. Rev. B **79**, 195208 (2009).
- ⁴⁴Zhiyong Wang, Tao Lin, Peng Wei, Xinfei Liu, Randy Dumas, Kai Liu, and Jing Shi, Appl. Phys. Lett. **97**, 042112 (2010).
- ⁴⁵Y. H. Choi, N. H. Jo, K. J. Lee, J. B. Yoon, C. Y. You, and M. H. Jung, J. Appl. Phys. **109**, 07E312 (2011).
- ⁴⁶Chun-Rong Lin, Yu-Jhan Siao, Shin-Zong Lu, and Chie Gau, IEEE TRANSACTIONS ON MAGNETICS **45**,4275 (2009).
- ⁴⁷P. Terzieff and K.L. Komarek Monatshefte fur Chemie, **109**, 1037 (1978).